

# **TOPIC 18 — HL ACIDS/BASES**

## **18.1 — CALCS INVOLVING ACIDS AND BASES**

IB Chemistry  
T18D04



# 18.1 **Calculations involving acids and bases - 4 hours**

- 18.1.1 State the expression for the ionic product constant of water ( $K_w$ ). (1)
- 18.1.2 Deduce  $[H^+(aq)]$  and  $[OH^-(aq)]$  for water at different temperatures given  $K_w$  values. (3)
- 18.1.3 Solve problems involving  $[H^+(aq)]$ ,  $[OH^-(aq)]$ , pH and pOH. (3)
- 18.1.4 State the equation for the reaction of any weak acid or weak base with water, and hence deduce the expressions for  $K_a$  and  $K_b$ . (1)
- 18.1.5 Solve problems involving solutions of weak acids and bases using the expressions:  $K_a \times K_b = K_w$ ,  $pK_a + pK_b = pK_w$ ,  $pH + pOH = pK_w$ . (3)
- 18.1.6 Identify the relative strengths of acids and bases using values of  $K_a$ ,  $K_b$ ,  $pK_a$  and  $pK_b$ . (2)



## 18.1.1 – The water constant $K_w$

- 18.1.1 State the expression for the ionic product constant of water ( $K_w$ ). (1)
- When water is purified by repeated distillation its electrical conductivity falls to a very low (and constant) value
- This means that pure water dissociates to a small extent to form ions
  - $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$
  - $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$

From last class:

- $K_w = [\text{H}^+(\text{aq})] \times [\text{OH}^-(\text{aq})]$



## 18.1.1 – $K_w$ value

- This value of  $K_w$  is known as the **ionic product constant of water**.
  - @298K (25°C)  $K_w = 1 \times 10^{-14}$ 
    - $[H^+] = 1 \times 10^{-7}$
    - $[OH^-] = 1 \times 10^{-7}$
  - No matter the value of  $K_w$  (as it changes depending on the surrounding conditions), concentrations of  $[H^+]$  and  $[OH^-]$  will equal each other in pure water
  - If  $[H^+]$  of a solution goes up,  $[OH^-]$  must go down, and visa versa



## 12.1.2 – $K_w$ at different Temps

- 18.1.2 Deduce  $[H^+(aq)]$  and  $[OH^-(aq)]$  for water at different temperatures given  $K_w$  values. (3)

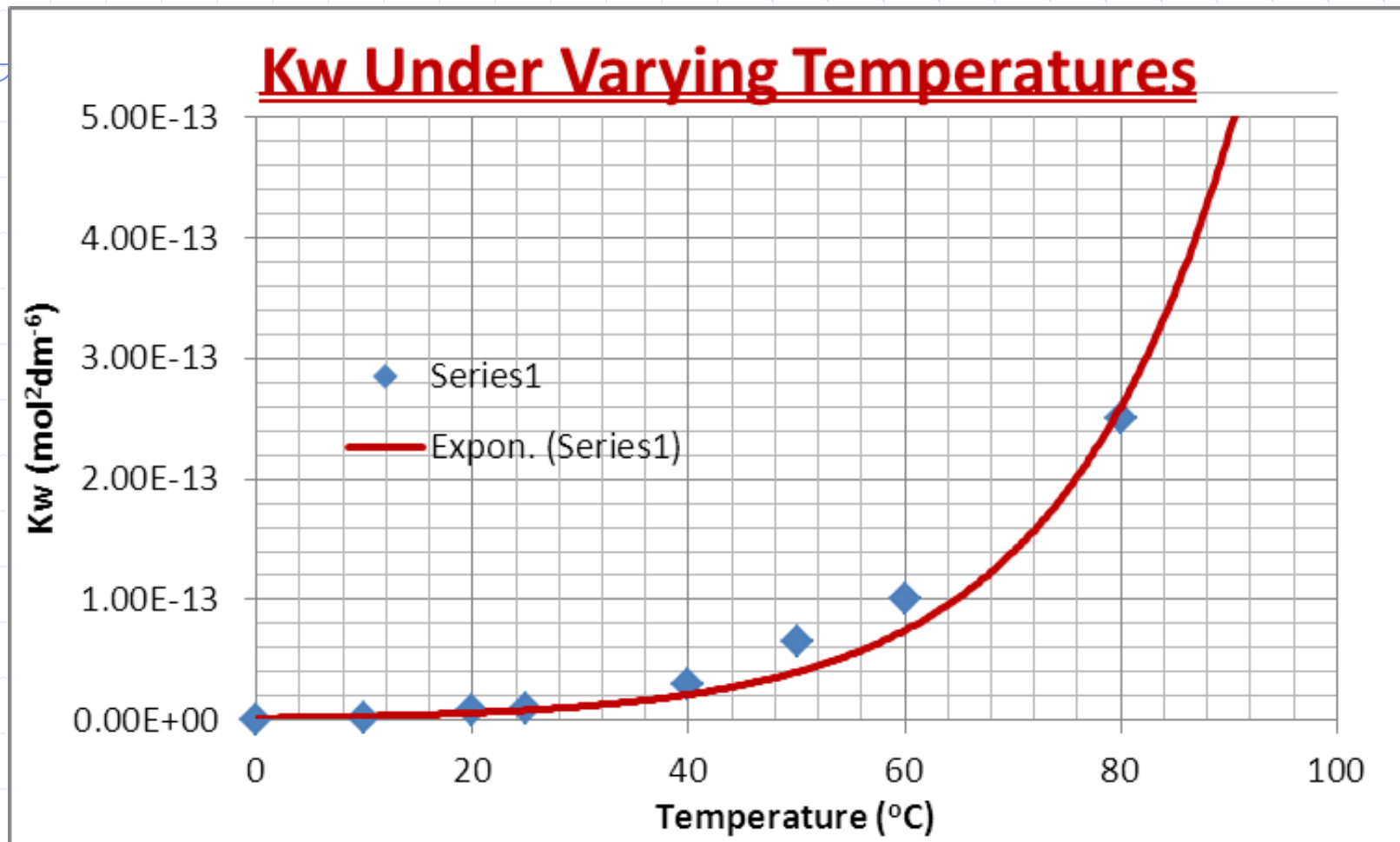
Temperature	0°C	25°C	40°C	100°C
$K_w$ (mol <sup>2</sup> dm <sup>-6</sup> )	$0.11 \times 10^{-14}$	$1.0 \times 10^{-14}$	$2.9 \times 10^{-14}$	$51.3 \times 10^{-14}$

- Water becomes increasingly dissociated and hence acidic as the temperature rises
- This accounts for the corrosive action of hot pure water on iron pipes:  $[H^+]$  ions increased



The concentrations of ions  $[H^+]$  and  $[OH^-]$  both increase equally, so the solution is neutral, but...

## 18.1.2 – $K_w$ changes!



## 18.1.2 – Enthalpy of Dissociation

- Dissociation of water is an Endothermic process:
  - Topic 05 – energy is needed to separate oppositely charged ions
  - Topic 07 – Le Châtelier's principle predicts that increasing the temperature will favor the reaction that absorbs the heat (negates change) in this case, the endothermic process
  - Increasing  $K_w$  values also tells that there is an increase in products of the equilibrium (more  $[H^+]$  and  $[OH^-]$ )



## 18.1.2 – Example: $K_w$ at 60°C

- At 60°C, the ionic product constant of water is  $9.6 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6}$ . Calculate the pH of a neutral solution at this temperature
  - Remember, what does neutral mean?
  - What equations will we use?





## 18.1.3 – Inverse Scales of pH/pOH

- 18.1.3 Solve problems involving  $[H^+(aq)]$ ,  $[OH^-(aq)]$ , pH and pOH. (3)
- This material was covered in SL Topic 08, for review please revisit those slides
- Conversions should be simple between:
  - pH
  - pOH
  - $[H^+]$
  - $[OH^-]$



## 18.1.3 – Calc Examples

- Calculate the pH of  $0.01 \text{ mol dm}^{-3} \text{ NaOH(aq)}$
- Calculate the pH of  $0.01 \text{ mol dm}^{-3} \text{ Ba(OH)}_2$
- Calculate the pH of  $0.01 \text{ mol dm}^{-3}$  sulfuric acid
  - Hint: think about the strong/weak properties of sulfuric acid and its conjugates as it's deprotonated
- A solution of  $\text{HNO}_3(\text{aq})$  contains 1.26g of the pure acid in every  $100\text{cm}^3$  of aqueous solution. Calculate the pH of the solution
- A solution of  $\text{NaOH(aq)}$  contains 0.40g in every  $50\text{cm}^3$  of aqueous solution. Calculate the pH of the solution



## 18.1.3 – pH of very dilute soln's

- Talbot brings up a good point, when calculating the pH of very dilute solutions of acid (say  $1.0 \times 10^{-8} \text{ mol dm}^{-3} \text{ HCl(aq)}$ ), students often run into the following problem:
  - ~~$-\log[1.0 \times 10^{-8}] = 8$~~  (but this value is basic??)
  - This does not take into account that there are two sources of  $\text{H}^+$  ions (the water and HCl)
    - $[\text{H}^+]_{\text{Total}} = [\text{H}^+]_{\text{H}_2\text{O}} + [\text{H}^+]_{\text{HCl}}$
  - At higher concentrations of acid, the  $[\text{H}^+]$  contribution from water is insignificant and can be neglected. But when  $[\text{H}^+] < 1.0 \times 10^{-6}$



- So for  $1.0 \times 10^{-8} \text{ mol dm}^{-3}$  HCl:

- $[H^+]_{\text{Total}} = [H^+]_{\text{H}_2\text{O}} + [H^+]_{\text{HCl}}$

- Let  $[H^+]_{\text{H}_2\text{O}} = y$

- Then OH is also,  $[OH^-]_{\text{H}_2\text{O}} = y$

- Substitute:

- $[H^+]_{\text{Total}} = [H^+]_{\text{H}_2\text{O}} + [H^+]_{\text{HCl}}$

- $[H^+] \times [OH^-] = 1 \times 10^{-14}$

- $[ [H^+]_{\text{H}_2\text{O}} + [H^+]_{\text{HCl}} ] \times [OH^-] = 1 \times 10^{-14}$

- $[ y + (1.0 \times 10^{-8}) ] \times [y] = 1 \times 10^{-14}$

- $y^2 + (1.0 \times 10^{-8})y - (1.00 \times 10^{-14}) = 0$

- Solve for  **$y = 9.5 \times 10^{-8} = [H^+]_{\text{H}_2\text{O}}$**

- $[H^+]_{\text{total}} = [H^+]_{\text{H}_2\text{O}} + [H^+]_{\text{HCl}} = 9.5 \times 10^{-8} + 1.0 \times 10^{-8}$

- **$[H^+]_{\text{total}} = 10.5 \times 10^{-8}$**

- **pH = 6.98** so the solution is weakly acidic

*Just for your  
info, to my  
knowledge this  
is not going to  
be a tested  
concept*



## 18.1.3 – Negative pH values

- The scale is 0-14, but negative and 14+ values are possible
- 12M HCl,  $\text{pH} = -1.1$  (Commercially available HCl)
- 10M NaOH,  $\text{pH} = 15.0$  (Saturated NaOH)
- There are some complications when it comes to calculations based on highly concentrated solutions
- We must think about the **effective concentration of ions** in solution, and not just those potentially in solution



Generally, calculations in IB Chemistry, especially on the IB exam, will be in the 0-14 range.

# 18.1 – Terms for AB Equilibrium

- **Acid ionization constant ( $K_a$ )** – equilibrium constant for the ionization of an acid.
  - $pK_a = -\log_{10} K_a$
- **Base ionization constant ( $K_b$ )** – equilibrium constant for the ionization of a base.
  - $pK_b = -\log_{10} K_b$
- **Ionic product constant for water ( $K_w$ )** – equilibrium constant for the ionization of water
  - $K_w = 1.0 \times 10^{-14}$  Only @25°C
  - $pK_w = -\log_{10} K_w$        $pK_w = 14$



# 18.1 – $K_a$ vs $pK_a$ and its conjugates

- $\text{HCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$ 
  - Strong acids have weak conjugate bases
  - Weak acids have strong conjugate bases
  - Strong bases have weak conjugate acids
  - Weak bases have strong conjugate acids

	<b>HCl(aq)</b>	<b>H<sub>2</sub>O(l)</b>	<b>H<sub>3</sub>O<sup>+</sup>(aq)</b>	<b>Cl<sup>-</sup>(aq)</b>
	Strong Acid	Weak Base	Strong Acid	Weak Base
	Large $K_a$	Small $K_b$	Large $K_a$	Small $K_b$
	Small $pK_a$	Large $pK_b$	Small $pK_a$	Large $pK_b$



# 18.1.4 – Acid Dissociation Constant

- A weak monobasic (monoprotic) acid, HA, reacts with water as follows:
  - $\text{HA(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$
- The equilibrium constant for this reaction
  - $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$
  - The  $K_a$  for a strong acid is obviously much larger than for a weak acid as the equilibrium is almost completely to the right ( $K_c$  is BIG)



$$K_{a(\text{strong})} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$K_{a(\text{weak})} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$



## 18.1.4 – $K_a$ to $pK_a$ Conversion

- $K_a$  values, because often small (for weak acids) can be represented as  $pK_a$  values
  - $-\log_{10} K_a = pK_a$
  - Smaller  $pK_a$  values are stronger
  - Bigger  $K_a$  values are stronger
  - Just like the pH scale, a change of 1 is a factor of 10; change of 2, a factor of 100
  - $K_a$  values for strong acids are not usually quoted as the reactions go to completion and approach infinity in dilute solutions.
  - Only changes in Temp affect the  $K_a$ ,  $K_b$ , or  $K_c$



# 18.1 – Finding pH of solutions

- For a **strong acid**, use the  $[H^+]$  and  $-\log$
- For a **strong base**, use the  $[OH^-]$  and  $14-(-\log)$
- For a **weak acid**, you must use the given value of  $K_a$  and the equilibrium expression

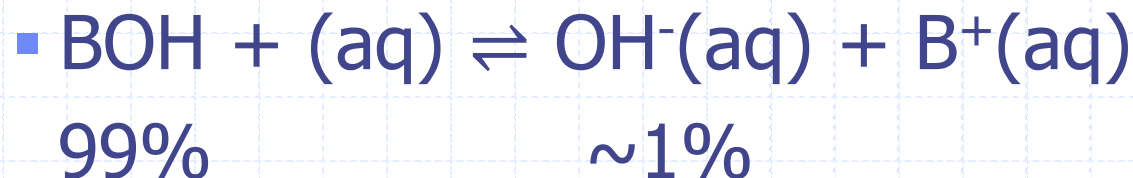
$$K_a = \frac{[ \quad ( \quad ) ] [ \quad ( \quad ) ]}{[ \quad ( \quad ) ]}$$

- For a **weak base**, you must use the given value of  $K_b$  and the equilibrium expression

$$K_b = \frac{[ \quad ( \quad ) ] [ \quad ( \quad ) ]}{[ \quad ( \quad ) ]}$$



- We make the assumption for weak acid and bases that the dissociated conjugate product concentrations are negligible (insignificant) compared to the original concentration of the reactant:



- This will make our calculations much easier, but we must first confirm this assumptions correctness

# 18.1 – I.C.E. charts

- In the calculations to follow we will use a very important chart that you've already been exposed to in HL equilibrium calculations
- The I.C.E. chart stands for:
  - I: Initial concentration
  - C: Change in concentration
  - E: Equilibrium concentration

$$K_c = \frac{[ ]}{[ ] [ ]}$$

	Acid or Base	+ ion	- ion
Initial	Initial concentration	0	0
Change	- x	+ x	+ x
<b>Equilibrium Conc</b>	<b>c - x</b>	<b>+ x</b>	<b>+ x</b>

# 18.1 – Ex #1 Solving for pH of weak acid

- Calculate the pH of a 1.00 mol dm<sup>-3</sup> aqueous solution of hydrofluoric acid, HF(aq), given that the acid dissociation constant for HF is 7.2x10<sup>-4</sup>
  - HF(aq) ⇌ H<sup>+</sup>(aq) + F<sup>-</sup>(aq)
  - $K_a = \frac{[ \quad ] [ \quad ]}{[ \quad ]}$

	HF(aq) mol dm <sup>-3</sup>	H <sup>+</sup> (aq) mol dm <sup>-3</sup>	F <sup>-</sup> (aq) mol dm <sup>-3</sup>
Initial	1.00	0	0
Change	- x	+ x	+ x
Equilibrium Conc	1.00 - x	+ x	+ x



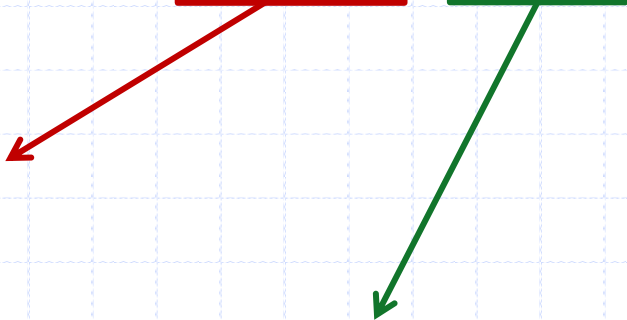
•  $K_a = \frac{[ \quad ]}{[ \quad ]}$

Now we make the assumption!  
That x is insignificant compared to the initial concentration! So 1.00-x =1.00

# 18.1 – Assumption Verified!

■  $K_a = 7.2 \times 10^{-4} = \frac{[ \quad ( \quad ) ] ( \quad )}{( \quad )} \quad [ \quad ]$

If no assumption, solve quadratic:  
 $x^2 + (7.2 \times 10^{-4})x - (7.2 \times 10^{-4} \times 1.00) = 0$   
 $ax^2 + bx + c = 0$   
 $a = 1$   
 $b = 7.2 \times 10^{-4}$   
 $c = -7.2 \times 10^{-4}$   
 $\frac{\sqrt{\quad}}{\quad} = 2.65 \times 10^{-2} = [H^+]$   
 $-\log[H^+] = \text{pH} = \mathbf{1.57}$



$$x^2 = 7.2 \times 10^{-4} \times 1.00$$
$$x = \sqrt{\quad}$$
$$x = 2.68 \times 10^{-2}$$
$$x = [H^+]$$
$$-\log[H^+] = \text{pH}$$
$$\text{pH} = \mathbf{1.57}$$



# 18.1 – Things to know about pK values

- $pK_a$  and  $pK_b$  numbers are usually positive w/o units
- Stronger acids or bases with high values for  $K_a$  or  $K_b$  have lower values for  $pK_a$  and  $pK_b$  respectively
- A change in one unit of  $pK_a$  or  $pK_b$  represents a 10-fold change in the value of  $K_a$  or  $K_b$
- $pK_a$  and  $pK_b$  must be quoted at a specific temperature, generally 25°C for standard conditions and measurements
- High values of  $K_a$  for an acid will have low values of  $K_b$  for its conjugate base (make sense?)



$$\text{■ } K_a \cdot K_b = [H^+][OH^-] = K_w$$

# 18.1 – Examples of Values for A/B

- As you can see, large  $K_a$  values result in smaller  $pK_a$  values:

Acid	Formula	$K_a$	$pK_a$
Methanoic	HCOOH	$1.8 \times 10^{-4}$	3.75
Ethanoic	CH <sub>3</sub> COOH	$1.8 \times 10^{-5}$	4.76
Propanoic	C <sub>2</sub> H <sub>5</sub> COOH	$1.4 \times 10^{-5}$	4.87

- The same is true for values of  $K_b$  and  $pK_b$ :

Base	Formula	$K_b$	$pK_b$
Ammonia	NH <sub>3</sub>	$1.8 \times 10^{-5}$	4.75
Methlyamine	CH <sub>3</sub> NH <sub>2</sub>	$4.6 \times 10^{-4}$	3.34
Ethylamine	C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	$4.5 \times 10^{-4}$	3.35





# 18.1 – Ex #2 Solving for $K_b$ of weak base

- Calculate the  $K_b$  for a  $0.100 \text{ mol dm}^{-3}$  aqueous solution of methylamine,  $\text{CH}_3\text{NH}_2$ , at  $25^\circ\text{C}$ . Its pH is 11.80 at this temperature
  - At  $25^\circ\text{C}$ ,  $\text{pH} + \text{pOH} = 14.00$ , so  $\text{pOH} = 2.20$
  - $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-2.20} = 6.30 \times 10^{-3}$
  - $\text{CH}_3\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$
  - $K_b = \frac{[\text{CH}_3\text{NH}_3^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{CH}_3\text{NH}_2(\text{aq})]}$

	$\text{CH}_3\text{NH}_2(\text{aq}) \text{ M}$	$\text{CH}_3\text{NH}_3^+(\text{aq}) \text{ M}$	$\text{OH}^-(\text{aq}) \text{ M}$
Initial	0.100	0	0
Change	- 0.00630	+ 0.00630	+ 0.00630
<b>Equilibrium</b>	<b>0.0937</b>	+ 0.00630	+ 0.00630

# 18.1 – Ex#2 Finding $K_b$ answer

■  $K_b = \frac{[ \quad ( \quad ) ] \quad ( \quad )}{( \quad )} \quad \underline{\hspace{2cm}}$



# 18.1 – Ex #3 Solving for pH of weak base

■ A 0.20 mol dm<sup>-3</sup> aqueous solution of ammonia has K<sub>b</sub> of 1.8x10<sup>-5</sup> at 25°C, what is the pH?



▪ 
$$K_b = \frac{[ \quad ] [ \quad ]}{[ \quad ]}$$

	HF(aq) mol dm <sup>-3</sup>	H <sup>+</sup> (aq) mol dm <sup>-3</sup>	F <sup>-</sup> (aq) mol dm <sup>-3</sup>
Initial	0.20	0	0
Change	- x	+ x	+ x
Equilibrium Conc	0.20 - x	+ x	+ x

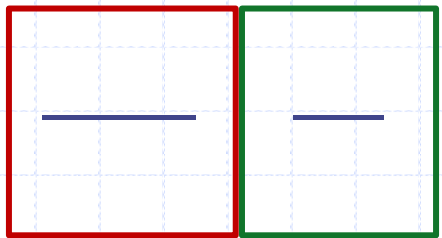
▪ 
$$K_b = \frac{[ \quad ]}{[ \quad ]}$$

Now we make the assumption!  
That x is insignificant compared to the initial concentration! So 1.00-x =1.00



# 18.1 – Ex#3 pH of weak base

■  $K_b = 1.8 \times 10^{-5} = \frac{[ \quad ( \quad ) ] ( \quad )}{( \quad )} \frac{[ \quad ]}{[ \quad ]}$



We have already proved that the assumption works so long as the value of  $K_b$  (or  $K_a$ ) is significantly less than the concentration of the base or acid. The general rule is 100 to 1000 times (or more) difference between the two and you're ok

$$x^2 = 1.8 \times 10^{-5} \times 0.20$$
$$x = \sqrt{\quad}$$
$$x = 1.9 \times 10^{-3}$$
$$x = [\text{OH}^-]$$
$$-\log[\text{OH}^-] = \text{pOH}$$
$$\text{pOH} = 2.72$$
$$\text{pH} = \mathbf{11.28}$$



Quadratic Calculator ☺